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13. ABSTRACT (Maximum 200 words) The fluorescence of global seawater has been investigated using a sensitive laser-induced fluorometry system. In surface seawater, fluorescence is low due to photochemical bleaching. Fluorescence intensity increases with increasing depth in the oceans to about 500 to 1000 m; below this depth, seawater fluorescence is generally constant. Sediment porewaters are much more fluorescent than the overlaying seawater. Both porewater fluorescence, and the dissolved organic carbon (DOC) concentration, increase with depth in the sediment. Fluorescence of porewaters can thus be used to provide an estimate of the DOC content. Because of the higher fluorescence in porewaters in comparison of seawater, fluorescence provides a means of estimating the amount of DOC diffusing out of sediments into seawater. The fluorescence measurements indicate that this source of DOC is only a minor contributor to the oceanic DOC budget.				
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January 22, 1996

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Reference: ONR N00014-89J-1422
Principal Investigator: Jeffrey L. Bada

Dear Dr. Green:

Enclosed please find three copies of the Final Technical Report for the above referenced grant entitled "Investigation of Oceanic Organic Chemistry using State-of-the-Art Laser Based Analytical Techniques."

Sincerely,

A handwritten signature in cursive script that reads "Beth Gardella".

Beth Gardella
Business Officer

enc

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FINAL REPORT FOR GN00014-89-J-1422

INVESTIGATIONS OF OCEANIC ORGANIC CHEMISTRY USING STATE-OF-THE-ART LASER BASED ANALYTICAL TECHNIQUES

The long range objective of this research was to utilize state-of-the-art laser based techniques to measure seawater fluorescence. These measurements would then be used to enhance our understanding of the role of oceanic organic chemistry in the global carbon cycle.

A: Laser-Induced Fluorometry (LIF)

In order to carry out precise measurements of seawater fluorescence, we developed a highly sensitive laser-induced fluorometer. This system uses as an excitation source the 325-nm beam of a HeCd laser. The laser beam is focused with a spherical lens into a 100- μm fused silica optic fiber which is used to transport the excitation light directly into a flow-through cell. The flow-through cell consists of a 200- μm internal diameter fused silica capillary column with about 0.5 cm of the polyimide coating removed by carefully scraping with a razor blade. Samples were delivered directly into the column using an injection valve and a high pressure pump is used to maintain a flow (0.5 ml min^{-1}) of 0.5 M NaCl through the column. The emission light is collected using 600- μm fused silica optic fibers positioned at right angles to the excitation beam. The emission light was first passed through a 400-nm high-pass cutoff filter and then into a grating monochromator set at 450 nm with a 10-nm slit. The exiting light is then collected using a photomultiplier tube, and the resulting current is converted to voltage with a preamplifier, which is then measured using a chart recorder. This LIF system has a detection limit of about 10 attomoles (10^{-17} moles) of pterin and eliminates internal quenching in highly fluorescent samples such as anoxic porewaters encountered when using conventional fluorometry.

B: Oceanic Fluorescence

Using laser-induced fluorometry, we studied the fluorescence of seawater and sediment porewater samples collected from throughout the global oceans. These measurements have provided a general understanding of the overall fluorescent budget and the processes controlling seawater fluorescence (1). In the open ocean, fluorescence and the concentration of dissolved organic carbon (DOC) are inversely correlated. Seawater fluorescence in the ocean is low in surface waters, increases with depth to about 500-1000 m, and is nearly constant in deep waters. Photochemical degradation in surface waters, release from particles during nutrient regeneration in mid-depth waters, and the slow *in situ* formation in deep waters control oceanic fluorescence profiles. On a local scale, profiles may be affected by diffusion from anoxic sediments (2,3). The characterization of the molecules responsible for seawater fluorescence has been investigated using high performance liquid chromatography (HPLC) coupled with LIF detection (4, 5). Seawater fluorescence is primarily due to humic substances which make up roughly 60 % of

the total dissolved organic carbon (DOC) present in seawater. The turnover time of the fluorescent material in the oceans is about 2000 to 4000 years.

The fluorescence in anoxic porewaters is directly correlated with the DOC concentration and the fluorescence intensity in porewaters provides a good estimate of the DOC concentration (2,3). Because porewaters are much more fluorescent than seawater, fluorescence measurements near the seawater/sediment interface provide a direct way of assessing whether the release of DOC from sediments to the water column is a contributor to the DOC pool in the oceans (2,3).

One area where we found seawater fluorescence to be different than in other oceanic regions is the Arctic Ocean, one of the least studied regions with respect to oceanic organic chemistry. The reason for this lack of information for the Arctic Ocean is simple: sampling a permanently ice covered ocean is logistically difficult. As a result, virtually nothing is known about the cycling of DOC in the Arctic Ocean. We have recently made fluorescence measurements of Arctic Ocean seawater collected through the ice in a region on the continental shelf 25-50 km north of Prudhoe Bay, Alaska. The fluorescence signal in this area is greater than in other near-shore regions that we have investigated. **Figure 1** shows the fluorescence measurements at the Arctic Ocean near-shore locality compared to that at near-shore stations off Southern California. The reason of the higher fluorescence in the

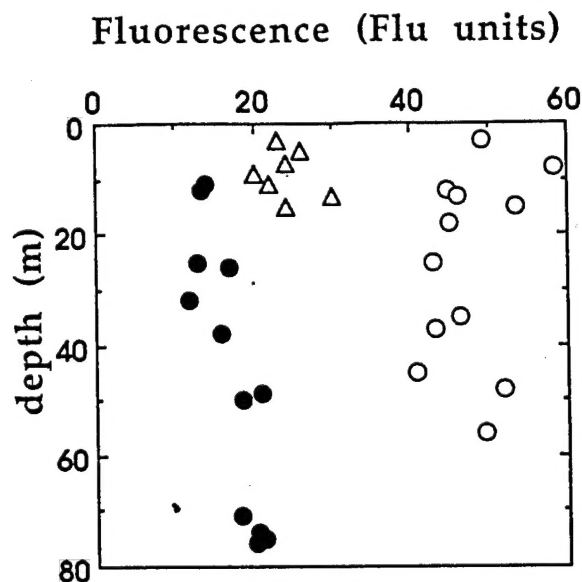


Figure 1: Seawater fluorescence in the ice covered Arctic Ocean 25-50 km north of Prudhoe Bay, Alaska (O); in the San Clemente Basin, Southern California (●); and in the kelp-beds off La Jolla (Δ).

Arctic Ocean seawater is unclear at this point, but may be due to the ice layer providing protection from photochemical degradation which is responsible for the low fluorescence in the surface waters in ice-free oceanic regions. This surmise should be testable by collecting Arctic Ocean seawater samples in ice-free areas during the summer and comparing the fluorescence of these samples with those collected during ice covered periods. If fluorescence is indeed lower during the

summer, than by studying the change in seawater fluorescence as the ice cover melts, we could accurately determine the rate constant for the photochemical degradation of seawater fluorescence, which so far has only been estimated from experiments carried out in the laboratory (1).

C. Development of an *in situ* LIF system

All of these previous studies of seawater fluorescence used water samples collected at sea, which were returned to the laboratory of analysis. One potential drawback with this methodology is that it precludes real-time monitoring of the fluorescent, and thus certain organic, components in seawater. In order to develop potential techniques for measuring fluorescence in real-time while at sea, we constructed an *in situ* LIF system which used a quartz fiber optic cable to deliver an excitation laser pulse to a submersible flow through cell and a fused silica fiber optic cable to collect and transmit the fluorescence back to a detector on board ship (6). A 337 nm pulsed N₂ laser was used for excitation. Using band pass filters, the emitted light between 400 and 500 nm was sent to photomultiplier/divider system which was used to compare the emission signal to a reference signal. The fluorescence signal was collected on a recorder, and an oscilloscope which was interfaced with a computer for data collection and analysis. The *in situ* probe consisted of a flow-through cell which contained the fibers, and a pump to flow seawater through the cell. The probe was suspended on a hydrowinch and lowered off the ship. Figure 2 shows the *in situ* fluorescence measurements carried out in San Diego Bay and at

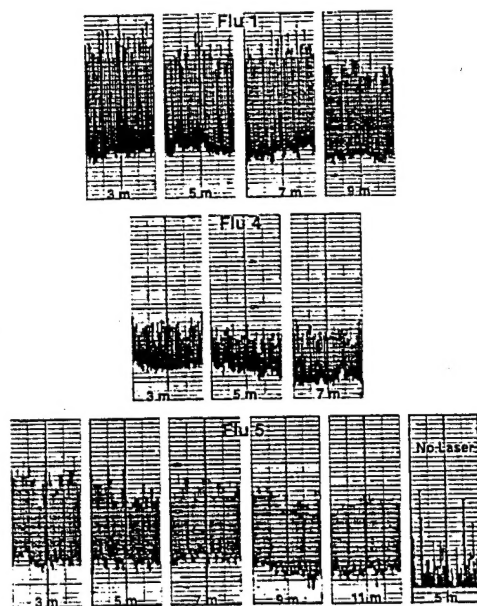


Figure 2: *In situ* seawater fluorescence measurements made during 23-24 March 1993. The height of the signal gives the fluorescence intensity. Each panel represents 2 minutes (120 laser shots) of continuous measurements. FLU-1 is in San Diego Bay located about 100 m off Harbor Island. FLU-4 is at the entrance to San Diego Bay. FLU-5 is in a kelp-bed about 1 km off La Jolla.

near coastal stations during a cruise in March, 1993. The *in situ* values in general agreed well with those obtained from samples collected at sea and measured later in the laboratory. Significant differences in fluorescence at the three stations were found using *in situ* fluorometry. The large fluorescence signal at the kelp-bed FLU-5 station is interesting and suggests that there may be a biological fluorescence component associated with this environment in comparison to the open ocean. During the March 93 cruise we were unable to measure the *in situ* fluorescence at a more open ocean locality because of equipment problems.

The *in situ* LIF system we developed has several advantages over a totally submersible *in situ* instrument. Our system is easily deployed at sea because only the *in situ* sample cell needs to be lowered from the ship. The only power that is required is that needed to run the submersible pump. The cost of the system is relatively inexpensive because there is no need for a large, bulky pressure housing unit. Finally, the most expensive part of the system (e. g., the laser and detector) remain on board ship and thus the only thing that might be lost over the side is the *in situ* probe. The main drawback of our design is that the transmission loss of UV excitation pulse caused by impurities in the quartz optic fiber limits the depths at which measurements can be carried out to the upper 100 m of the ocean. Improvements in the purity of quartz optic fibers in the future would minimize this problem and allow the system to be used to monitor fluorescence at greater depths in the ocean.

New Oceanographic Sensors and Instruments

The *in situ* fluorometry system can be used for investigations of the fine-scale time and space variations of one of the components of the organic matter in the oceans. The instrument has potential wide-ranging applications for the real-time sensing of the oceans and other natural water bodies.

Significance of Research to ONR

As we advance into the next century, the application of state-of-the-art analytical techniques will permit ocean scientists to attain a new level of understanding of key oceanic processes. Laser based sensors such as the fluorometer proposed here will allow for novel studies of ocean chemistry not possible with conventional techniques. The *in situ* system that will be developed can be used to study a component of the oceanic DOC in real-time at sea. The successful development of this system will be a big step forward in bringing ocean scientists closer to the ocean rather than the usual method of bringing the ocean samples back to the laboratory for analysis.

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